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Relations between Diatomic Constants and the Features of the Potential Energy Surfaces

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The semiempirical method is used to calculate potential energy surfaces. The linear H_3 and rectangular H_4 systems have been chosen as standard surfaces in order to compare the surface features. Relationships between diatomic constants and topological features along a minimum energy path, and the height and location of the barrier, are demonstrated.

The knowledge of the relation between the effect of vibrational and translational energies on the reaction cross section and the topological features of potential energy surfaces have provided valuable information in understanding the fundamental nature of collision dynamics.[1-3] We are seeking additional insight into this relation. In this attempt, we investigate correlations between the features of the potential energy surfaces and the characters of the reactant molecules. With the understanding of the correlations, the effect of the two kinds of energies on the chemical reaction can be estimated directly from the characters of the reactant molecules.

Recently, more accurate ab initio potential energies have been calculated for many reaction systems, using fast computers. Even though the potential energies calculated by ab initio method are accurate, it is difficult to relate the potential energies with the character of reactant molecules because of the complicated calculation method. On the other hand, a semiempirical method can relate directly the potential energies with the character without complicated calculations. Commonly used semiempirical methods[4,8,10] employ the diatomic constants as the characteristics of reactant molecules.

This report investigates the relation between diatomic constants and features of potential energy surfaces, using our semiempirical method.[5] In this article, such simple models as linear H_3 and rectangular H_4 will be chosen. Varying the values of the diatomic constants which are used to calculate potential energies in the both systems, we observe the changes of the topological features along minimum energy path, and height and location of the barrier.

Theoretical

Our semiempirical method[5] to calculate potential energies (E) is based on a valence bond treatment[6] of an n-electron n-atom system. In this method, E can be obtained from the secular equation,

$$|\boldsymbol{H} - \boldsymbol{M}E| = 0 \qquad (1)$$

where $\boldsymbol{H}$ is a Hamiltonian matrix and $\boldsymbol{M}$ is an overlap matrix. Each matrix element is defined as

$$\begin{aligned} H_{ij} &= \sum \varepsilon_P \langle \Omega | H | P\Omega \rangle \langle \theta_i | P\theta_j \rangle, \\ M_{ij} &= \sum \varepsilon_P \langle \Omega | P\Omega \rangle \langle \theta_i | P\theta_j \rangle, \end{aligned} \qquad (2)$$

where H is the Hamiltonian of the system, P is a permutation operator of electrons, ε_p is the parity, and θ_i is the spin function.

The matrix elements of $\boldsymbol{H}$ contain multiple exchange integrals given by

$$\Lambda_p = \langle \Omega | H | P\Omega \rangle. \qquad (3)$$

We found that Λ_p is reduced to two basic types.[5] One of them is a transposition type, and the other is a cycle type. These integrals can be formulated in terms of diatomic components α_i, Q_i, and S_i, using the Mulliken approximation,[7] as follows;

$$\begin{aligned} \Lambda_P^1 &\simeq \Pi\, S_i^2[\sum (\alpha_i/S_i^2) + Q - \sum Q_i], \\ \Lambda_P^2 &\simeq (1/2)\Pi\, S_i[\sum (\alpha_i/S_i^2) + 2Q - \sum Q_i], \end{aligned} \qquad (4)$$

where Q is a Coulomb integral, which is expressed by the diatomic Coulomb integrals Qi, and i shows pairs formed with electrons (atoms). Since the multiple exchange integral Λ_P consists of these Λ_P^1 and Λ_P^2 the calculation of Λ_P is to evaluate the diatomic components α_i, Q_i, and S_i. The first two diatomic components α_i and Q_i are evaluated from the Morse and anti-Morse functions which contain diatomic constants:[8,10] dissociative energy D, force constant α, and internuclear equilibrium distance R_e. These diatomic constants are combined with spectroscopic information on diatomic molecules.[9] The last diatomic component S_i is formulated empirically with adjustable parameters κ and λ.

$$S_i = (1 + R_i\zeta_i + \frac{1}{3}\zeta_i^2 R_i^2)\exp(-\zeta_i R_i), \qquad (5)$$

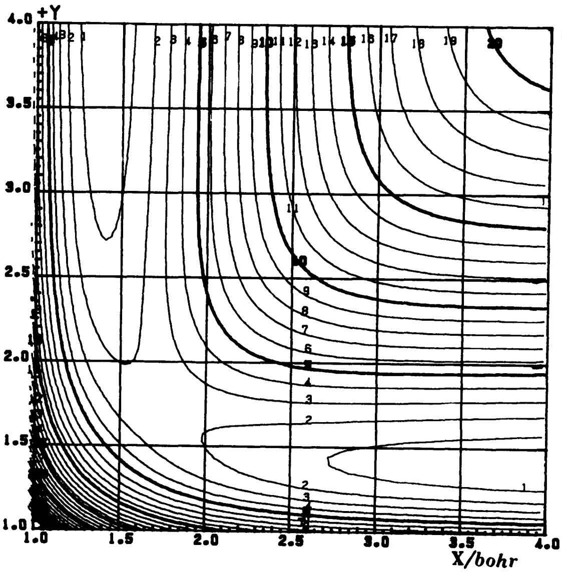
where the screening parameter ζ_i is given by[10,11]

$$\zeta_i = 1.0 + \kappa \exp(-\lambda R_i). \qquad (6)$$

Thus the potential energy E takes the following analytical form of coordinates of internuclear distance R as

$$E = f(\chi, \beta : R), \qquad (7)$$

with the adjustable parameter β and diatomic constants χ which are abbreviations for κ, λ and for D, α, R_e, respectively.



CONTOUR LINE VALUE

NC	VC
1	0.40000E-01
2	0.80000E-01
3	0.12000E+00
4	0.16000E+00
5	**0.20000E+00**
6	0.24000E+00
7	0.28000E+00
8	0.32000E+00
9	0.36000E+00
10	**0.40000E+00**
11	0.44000E+00
12	0.48000E+00
13	0.52000E+00
14	0.56000E+00
15	**0.60000E+00**
16	0.64000E+00
17	0.68000E+00
18	0.72000E+00
19	0.76000E+00
20	**0.80000E+00**
21	0.84000E+00
22	0.88000E+00
23	0.92000E+00
24	0.96000E+00
25	**0.10000E+01**
26	0.10400E+01
27	0.10800E+01
28	0.11200E+01
29	0.11600E+01
30	**0.12000E+01**

Fig. 1. Equipotential contour maps for H_3 surface corresponding to linear arrangement of the three atoms. The contour intervals are 1/25 of the H_2 dissociation energy. Number and value of the contour line are denoted by NC and VC, respectively.

In order to investigate the relationships between diatomic constants and the feature of potential energy surfaces, we define the surfaces by equipotential contour maps. The character of the surfaces are interpreted from the three following points of view;

1) Height, depth, and slope of the valley along the minimum energy path,

2) Height and location of the barrier,

3) Shape and passing positions of the minimum energy path.

Results

Equipotential contour maps for the linear H_3 and rectangular H_4 systems are presented in Figs. 1 and 4 as standard surfaces to compare the surface features. In order to assess the nature of these surfaces, we have changed the diatomic constants which are used to calculate the potential energies.[11,14] In six cases of diatomic constant change, the contour maps (a)—(f) are shown in both Figs. 3 and 5. The increase and decrease of the D, α, and R_e correspond to the cases of (a) and (b), (c) and (d), and (e) and (f), respectively. The barrier heights and the coordinates along the minimum energy path, at the starting point (entrance valley), at the saddle point (barrier), and at the ending point (exit valley), are presented in Tables 1 and 2, for each of six cases.

1) **Model of Linear H_3 System.** Figure 1 and Fig. 2 show equipotential contour maps for H_3 surfaces corresponding to a linear arrangement of the three hydrogen atoms calculated by our method[11] and the Truhlar-Horowitz method.[12,13]

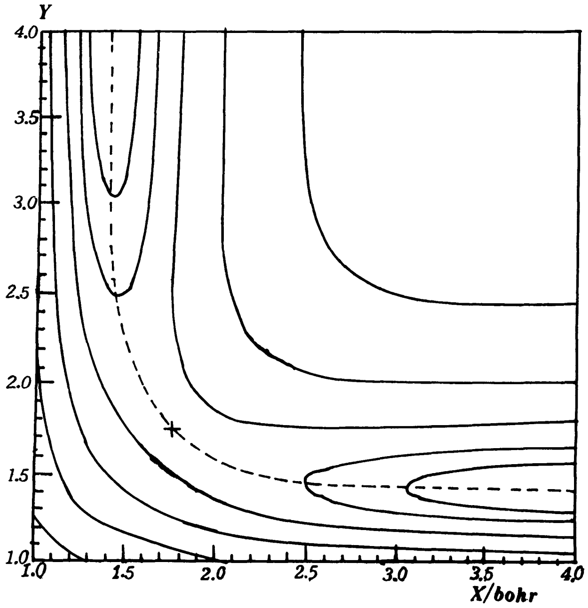
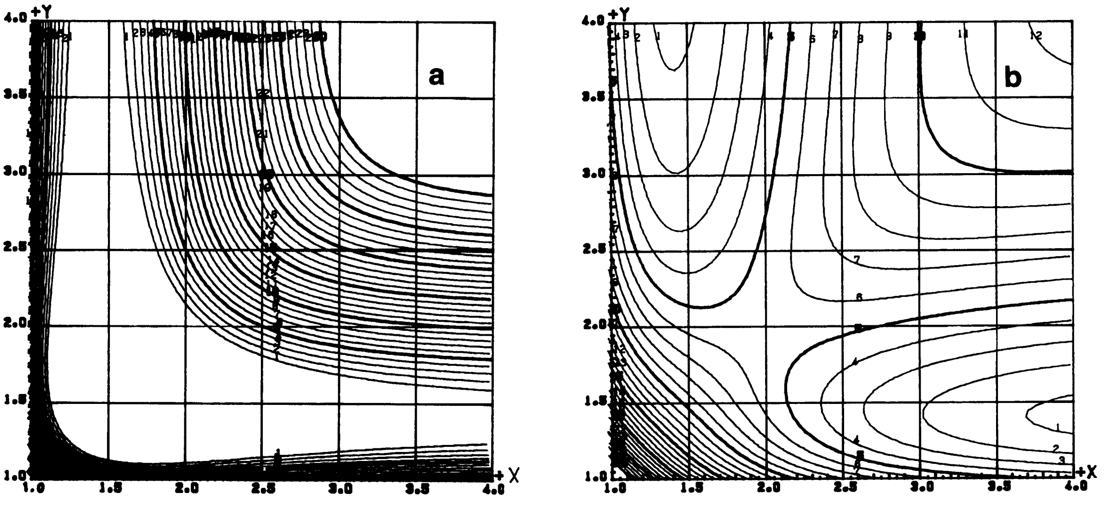
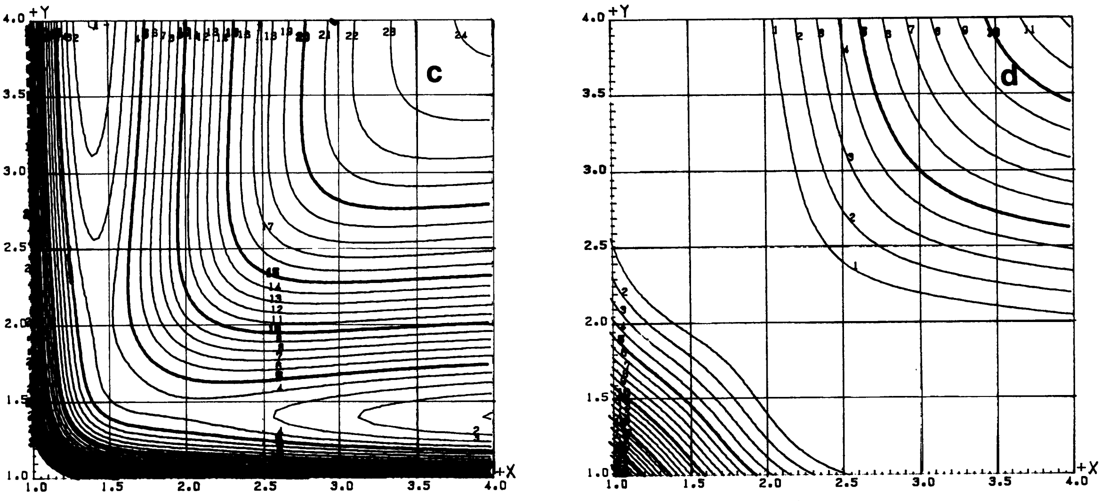


Fig. 2. Truhlar-Horowitz contour map for linear arrangement H_3 surface. The solid curves are cotours of the interaction potential corresponding to 3, 6, 12, 24, 48, 96, and 192 kcal mol^{-1}. The dashed curve is a minimum energy path and the cross is a saddle point.

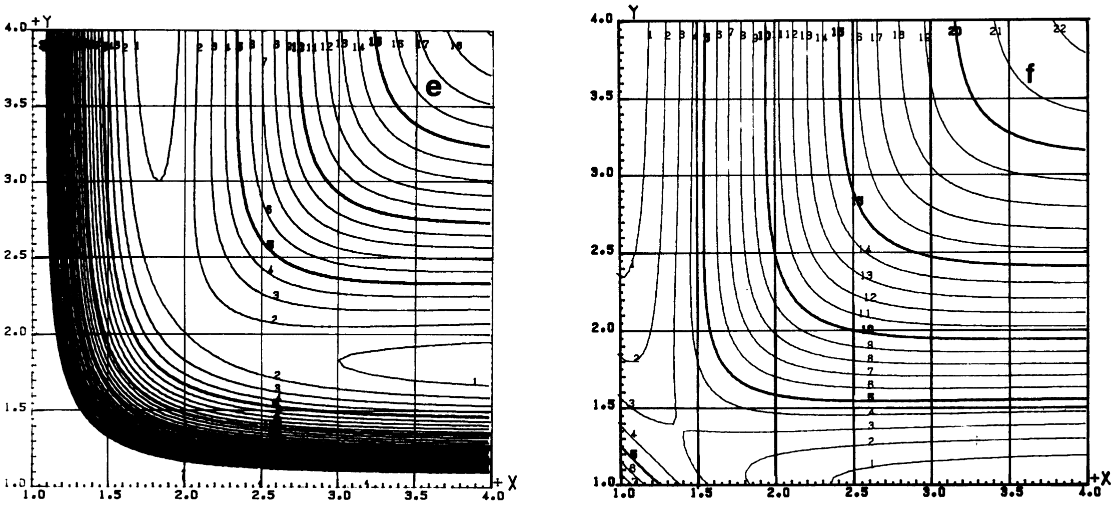
The values of the diatomic constants D, α, and R_e are 0.174475 a.u., 1.05 a.u.,$^{-1}$ and 1.401 bohr, respectively. The adjustable parameters κ and λ in Eq. 6 have been so determined that the barrier height calculated by using Eq. 7 agrees with that calculated by Liu[12]; that is $\kappa=3.20$ and $\lambda=1.202$.[11] In Table 1, the values of the barrier height and coordinates of the minimum energy path are shown together with the results of Liu. Comparisons of the minimum energy path, contour



(a) D=0.35 (b) D=0.10



(c) α=1.50 (d) α=0.60



(e) Re=1.80 (f) Re=1.00

Fig. 3. Equipotential contour maps on different D, α, R_e for model of the linear H_3 system.

line, and barrier height between Figs. 1 and 2 are satisfactory.

The changes of the features of the maps can be read off from Fig. 3 and Table 1 in the case of (a)—(b) as follows;

(a) D=0.35: The valley along the minimum energy

Table 1. Barrier Height and Coordinates of the Minimum Energy Path in Six Cases[a] of the Changes of Diatomic Constants for the Model of Linear H_3 System

Case	Starting point	Saddle point	Barrier height	Ending point
	bohr	bohr	kcal/mole^{-1}	bohr
H_3[b]	(4.00, 1.40)	(1.757, 1.757)	9.802	(1.40, 4.00)
H_3[c]	(4.00, 1.40)	(1.743, 1.743)	9.802	(1.40, 4.00)
(a)	(4.00, 1.40)	(1.60, 1.60)	(−38.83)	(1.40, 4.00)
(b)	(4.00, 1.60)	(1.90, 1.90)	24.49	(1.60, 4.00)
(c)	(4.00, 1.40)	(1.60, 1.60)	15.83	(1.40, 4.00)
(d)	(4.00, 1.40)	(2.05, 2.05)	(−1.46)	(1.40, 4.00)
(e)	(4.00, 1.90)	(2.10, 2.10)	7.35	(1.90, 4.00)
(f)	(4.00, 1.275)	(1.675, 1.675)	13.12	(1.275, 4.00)

a) See the text. b) Results of this Liu; Ref. 12. c) Results of this study; Ref. 11.

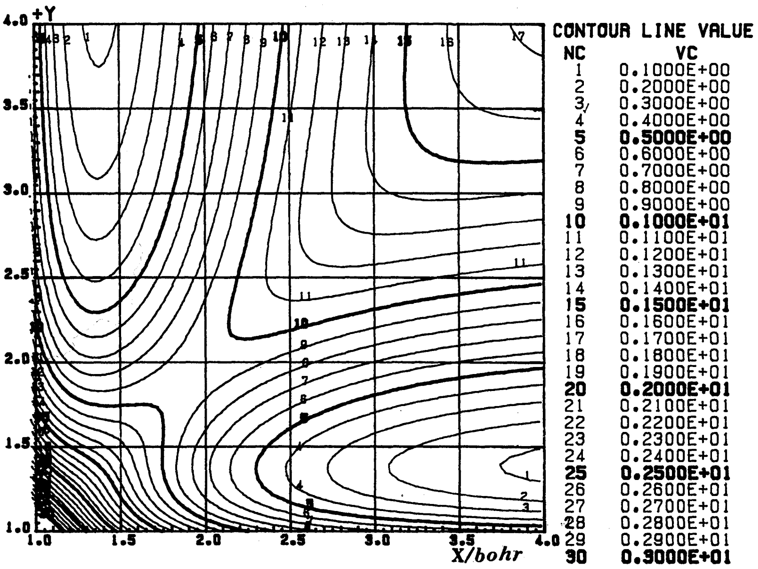


Fig. 4. Equipotential contour maps for H_4 surface corresponding to rectangular arrangement of the four atoms. The contour intervals are 1/10 of the H_2 dissociation energy. Number and value of the contour line are denoted by NC and VC, respectively.

path greatly increases in height, depth, and slope. The path moves to the inside. A deep ditch arises along the path.

(b) D=0.10: The valley along the minimum energy path decreases in height, depth, and slope, but the slope toward the barrier becomes steeper. The saddle point moves to the outside. The barrier height increases reasonably in value.

(c) α=1.50: The valley along the minimum energy path shallows but the slope becomes steep. The saddle point moves also to the inside. The basin lies between (2.0, 1.5) and (1.5, 2.0). The potential energy at the bottom in the basin is 16.87 kcal (1 cal=4.184 J) and is 15.83 kcal around the basin.

(d) α=0.60: There is no barrier but a ditch, and the slope becomes low-pitched along the minimum energy path.

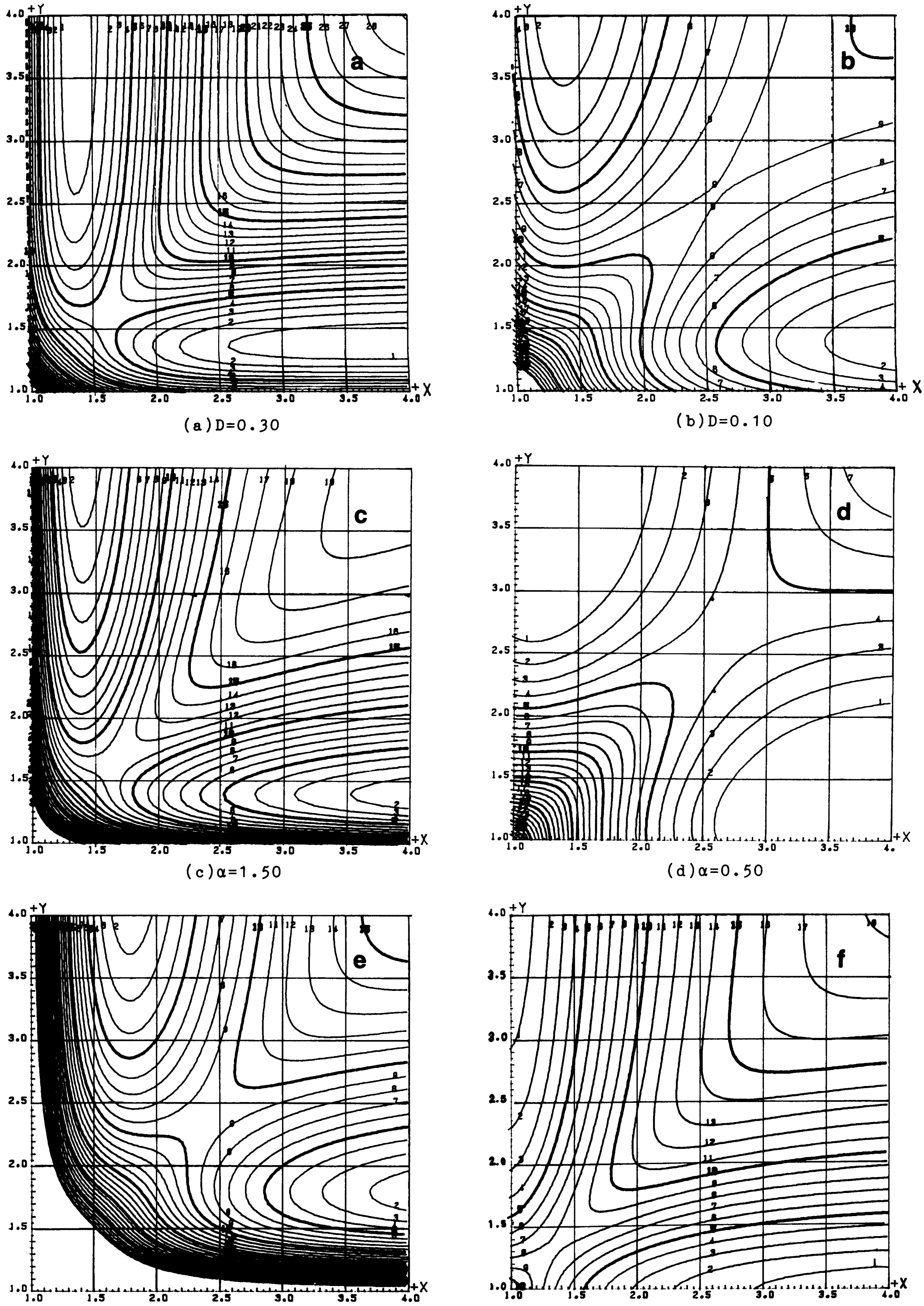
(e) R_e=1.80: The depth and slopes of the valley change very little, but the minimum energy path shifts to the outside.

(f) R_e=1.00: The depth and slopes of the valley change very little, but the minimum energy path shifts to the inside.

2) **Model of rectangular H_4 System.** Figure 4 shows equipotential contour maps for H_4 surfaces corresponding to a rectangular arrangement of the four atoms calculated by our method.[14] The values of the diatomic constants D, α, and R_e are 0.174475 a.u., 1.05 a.u.$^{-1}$, and 1.401 bohr, respectively. The adjustable parameters κ and λ in Eq. 6 have been so determined that the barrier height calculated by using Eq. 7 agrees with that calculated by Bender and Schaefer III[15]; that is κ=1.00 and λ=0.40.[11] The contour maps for rectangular H_4 system were calculated from the various semiempirical methods by Silver and Brown[16]

The changes in the features of the maps can be read off from the Fig. 5 and Table 2 in the case of (a)—(b) as follows;

(a) D=0.30: The valley along the minimum energy path increases in height, depth, and slope. The saddle



(a)D=0.30

(b)D=0.10

(c)α=1.50

(d)α=0.50

(e)Re=1.80

(f)Re=1.00

Fig. 5. Equipotential contour maps on different D, α, R_e for model of the rectangular H_4 system.

point moves to the inside. The barrier height decreases a little.

(b) D=0.10: The valley along the minimum energy path decreases in height, depth, and slope. The barrier height changes very little.

(c) α=1.50: The valley along the minimum energy

Table 2. Barrier Height and Coordinates of the Minimum Energy Path in Six Cases[a)] of the Changes of Diatomic Constants for the Model of Linear H_4 System

Case	Starting point bohr	Saddle point bohr	Barrier height kcal/mole^{-1}	Ending point bohr
H_4[b)]	(4.00, 1.40)	(2.10, 2.10)	114.11	(1.40, 4.00)
(a)	(4.00, 1.40)	(1.70, 1.70)	92.58	(1.40, 4.00)
(b)	(4.00, 1.50)	(2.65, 2.65)	97.41	(1.50, 4.00)
(c)	(4.00, 1.40)	(1.80, 1.80)	145.48	(1.40, 4.00)
(d)	(4.00, 1.30)	(2.70, 2.70)	45.00	(1.30, 4.00)
(e)	(4.00, 1.80)	(2.50, 2.50)	104.90	(1.80, 4.00)
(f)	(4.00, 1.00)	(1.60, 1.60)	116.95	(1.275, 4.00)

a) See the text. b) Results this study; Ref. 14.

path shallows and the slope becomes steep. The saddle point moves also to the inside.

(d) α=0.50: The depth and width of the valley increases and their slopes become very low-pitched along the minimum energy path.

(e) R_e=1.80: The depth and slopes of the valley changes very little, but the minimum energy path shifts to the outside. The barrier height changes a little.

(f) R_e=1.00: The depth and slopes of the valley change very little, but the minimum energy path shifts to the inside. The barrier height changes a little.

Conclusions

As is evident from the Figs. 3 and 5, the diatomic constants have sensitive effects on the features of the potential energy surfaces. Except for the case (c) in Fig. 3 where the basin is formed near the saddle point, it should be noted that there appears common outcomes on both cases of the linear H_3 and the rectangular H_4 systems as follows:

(1) The binding energy D correlates remarkably well with the depth, height and slope of the valley along the minimum energy path.

(2) The force constant α correlates especially well with the slope of the valley.

(3) The internuclear equilibrium distant R_e correlates explicitly with the position of the minimum energy path.

Finally, the next step is to investigate for a more complicated system the relationships between the diatomic constants and the curvature of the minimum energy path or position of the saddle point.

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